Appendix A. Quality Assurance Project Plan, Technical Background Document: Mercury Wastes, Evaluation of Treatment of Bulk Elemental Mercury, Final Report

February 8, 2002

Submitted to:

U.S. Environmental Protection Agency
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Submitted by:

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EPA Contract No. 68-W-98-025
Work Assignment No. 3-8

SAIC Project No. 06-0758-08-1373-000

QUALITY ASSURANCE PROJECT PLAN

TECHNICAL SUPPORT FOR AMENDMENT OF LAND DISPOSAL RESTRICTIONS FOR MERCURY WASTES

SAIC/EPA Prime Contract No. 68-W-98-025
Work Assignment WA#2-15

Submitted to:
Mary Cunningham, EPA Task Order Manager
Office of Solid Waste
U.S. Environmental Protection Agency

Submitted by:

ALTER Corporation

December 2000

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1.0 Project Description

1.1 Purpose

There are concerns about incineration of mercury-containing wastes since incineration does not destroy, extract, or immobilize mercury. It may actually increase rather than minimize mercury movement into the environment by releasing mercury vapor and mercury salts into the atmosphere. The Environmental Protection Agency Office of Solid Waste (EPA-OSW) in collaboration with the Accelerated Life Testing and Environmental Research Corporation (ALTER) is investigating alternative non-combustion technologies for the disposal of mercury-containing wastes.

The purpose of this project is to create a surrogate mercury sludge and to investigate a range of commercial remediation technologies using a surrogate mercury sludge.

1.2 Process Description

A laboratory scale surrogate mercury sludge will be assembled by ALTER. The sludge will be characterized and subjected to leaching tests to provide baseline information.

Following analysis of the baseline data , the surrogate mercury sludge components will be shipped to commercial treatment vendors selected by Oak Ridge National Laboratory (ORNL) and EPA. The commercial vendors will mix and treat the surrogate sludge and return the treated material to ALTER for testing.

The vendor treated materials will be characterized and subjected to leaching tests to determine the applicability of the treatment processes.

1.3 Objectives

The objective of this investigation is to provide reliable information on the applicability of non-thermal alternative treatment technologies to treat mercury-containing wastes.

Primary objectives:

- Prepare a surrogate mercury sludge
- Characterize and determine the leachability of a surrogate mercury sludge under controlled laboratory conditions.
- Characterize and determine leachability of the treated surrogate mercury sludge.

2.0 Project Organization and Responsibility

2.1 Organizations Involved in the Project

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2.2 Quality Assurance Managers

1. Charles Sellers, Quality Assurance Officer, OSW, U.S.EPA
2. Rich Abitz, SAIC, Quality Assurance Officer for ALTER Corporation

The ALTER Quality Assurance officer will be responsible for data validation, investigation of “out of control” situations and the assurance that data quality checks are being made. Charles Sellers (EPA-OSW) will be responsible for reviewing the QAPP and providing comments to the project manager. The ALTER QA officer will review QA data from all contributing organizations. The ALTER QA officer is an essential link between all research members as data is developed, analyzed, reviewed and checked prior to reporting said work. These responsibilities are more specifically outlined in sections 6.0 and 8.0 of this document.

2.3 Responsibilities of Project Participants

Project organization and reporting relationships are depicted on the following chart. Josh Lewis (OSW), Mary Cunningham (OSW Task Order Manager), Charles Sellers (OSW QA Officer) and Sara Hartwell (SAIC) will be responsible for providing technical direction, project coordination and communication along with reviewing and approving the QAPP. Mike Morris, ORNL will be responsible for the statement of work for stabilization vendors, evaluation of vendor test plans and coordination of surrogate and vendor treated surrogate transfer between vendors and ALTER. Linda Rieser (ALTER, Subcontractor to SAIC) will serve as Project Manager and shall have responsibility for supervision and monitoring of all aspects of this project, including the collection of samples, sample custody, project planning, QAPP development, daily operations oversight, data analysis and will assist SAIC with final reports. Rich Abitz (SAIC) will serve as ALTER QA officer. Student research assistants and professional technicians will participate in the research under the guidance of the project manager. Student research assistants will primarily be involved in the laboratory work associated with leaching tests and will be responsible for monthly reports. Sara Hartwell, SAIC will be responsible for the final report.

Agvise Laboratory will provide support for characterization (Table 5.1). Environmental Enterprises will provide mercury analysis of surrogate, treated surrogate and leachates. The QA/QC control functions have been organized to allow independent review of project activities. The objective of the QA/QC efforts is to assess and document the precision, accuracy, and adequacy of the data derived from the investigation. Figure 2.1 shows project authority lines.

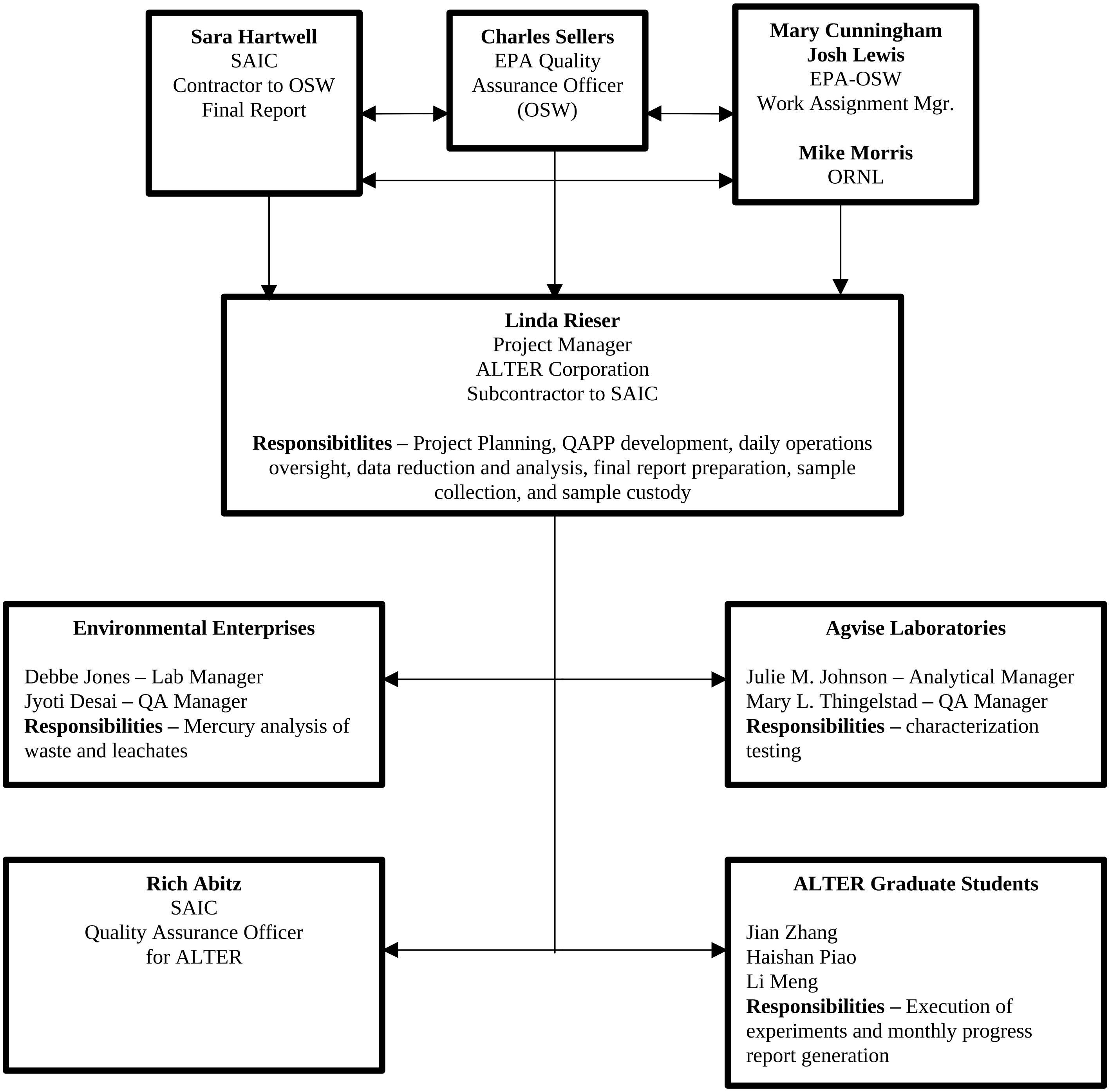


Figure 2.1 Project Organization

3.0 Experimental Approach

A surrogate mercury sludge will be constructed by ALTER for use in this evaluation. The surrogate will be subjected to physical and chemical characterization and leaching tests to determine leachability of the surrogate after treatment. The surrogate will be treated by vendors selected by ORNL and EPA's Office of Solid Waste. ALTER will ship two one-hundred pound samples to selected vendors for treatment and residuals return to ALTER. The surrogate will be shipped as pre-measured components to be blended by the vendors. Additional surrogate will be made available to the vendors upon request for pre-treatment treatability testing. ALTER will observe the mixing and treatment. Following successful treatment of the two one-hundred pound surrogate batches by the selected vendors, the entire 200 pounds of treated surrogate will be shipped to ALTER for sampling and evaluation. Physical and chemical characterization and leaching tests identical to those performed on the baseline surrogate will be performed on the vendor-stabilized materials. Figure 3.1 details the experimental design for this project. Appendix F provides the project schedule.

3.1 Construction of Surrogate Sludge

A surrogate sludge will be constructed for use in this study. The sludge composition is outlined in Table 3.1.

Table 3.1 Surrogate Sludge Composition

Sludge Constituent	Weight Percentage %	Mercury Concentration ppm
Phenyl Mercury	0.08	500
Mercury Nitrate	0.17	1000
Elemental Mercury	0.15	1500
Mercury Oxide	0.11	1000
Mercury Chloride	0.14	1000
Diatomaceous Earth	20	
Aluminum Hydroxide	10	
Ferric Chloride	10	
Sodium Chloride	10	
Motor Oil (new)	1	
Water	48.35	
Total	**100**	**5000**

Sludge will be mixed in 3 liter batches in a 5 quart Hobart mixer. Mercury species as listed in Table 3.1 will be added only after the major constituents have been well blended. Three random samples will be analyzed to assess total mercury variability and three TCLP tests will be performed to assess leachability. The laboratory scale surrogate will be characterized and leached as described in sections 3.2 and 3.3.

3.2 Characterization

Samples of the baseline surrogate, the vendor mixed surrogate before treatment and the treated surrogate will be analyzed for total mercury and subjected to the Toxicity Characteristics Leaching Procedure (TCLP). Samples of the sludge and leachate will be submitted to Environmental Enterprises Inc. for mercury analysis. Samples of the baseline surrogate and treated surrogate will also be sent to Agvise for physical and chemical measurements, including bulk density, moisture content, percent organic matter, cation exchange capacity, and particle size distribution. The Agvise testing uses standard methods for soils, established by the USDA and the Soil Society of America.

Additional characterization of the baseline surrogate and vendor stabilized materials by ALTER will include alkalinity and acidity testing, and pH analysis on all samples. All characterization testing will be performed in duplicate.

3.3 Leaching

In order to assess the stability of the wastes, several leaching procedures will be performed on the baseline surrogate and vendor treated surrogate. Leaching tests to be performed by ALTER include TCLP, and UC constant pH. Upon completion of each leaching test, the pH values will be taken by ALTER and the leachate mercury concentration will be determined by Environmental Enterprises Inc. All leaching tests will be performed with a minimum of 50% duplicates and will include an experimental blank. The following paragraphs discuss the leaching tests.

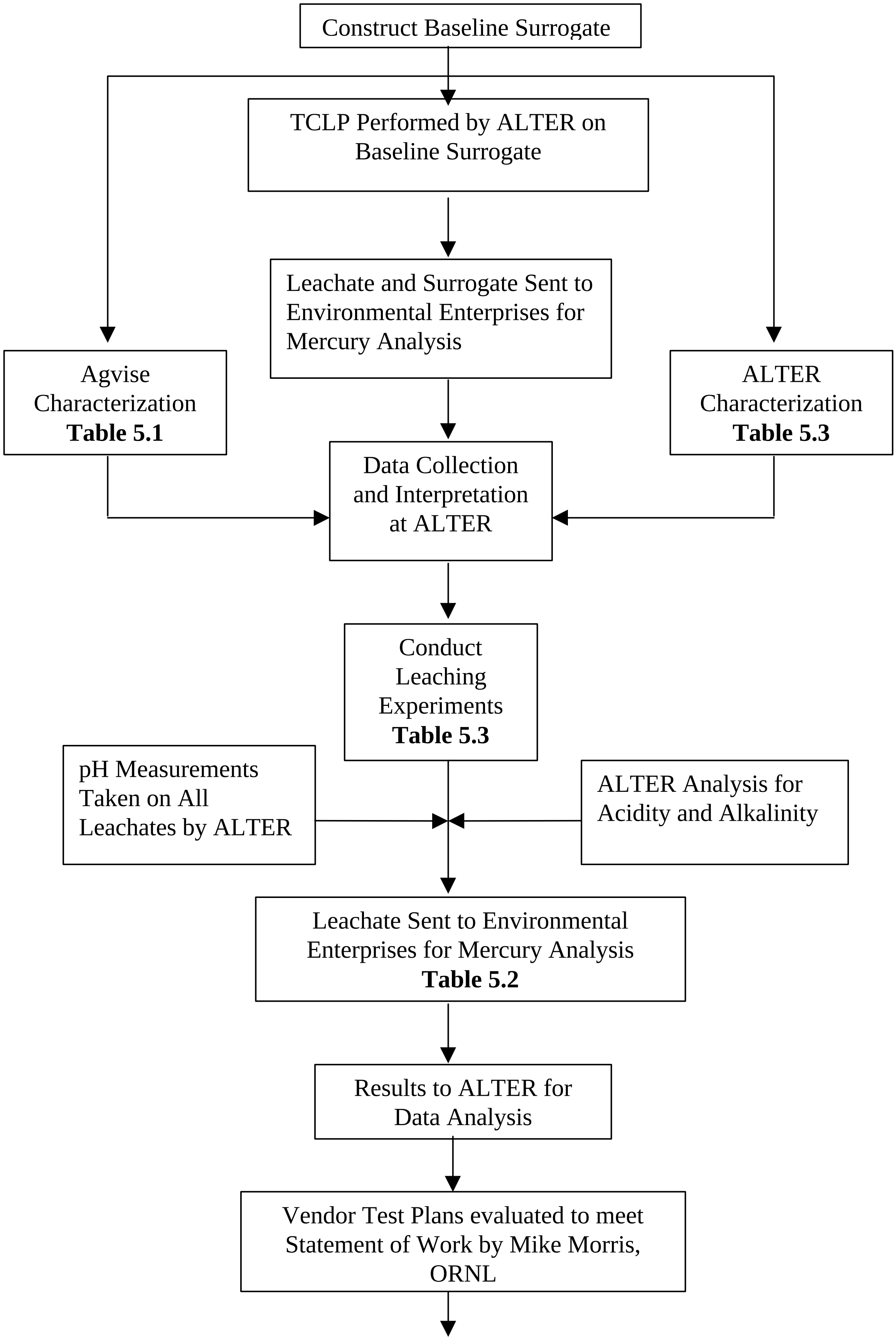
***Toxicity Characteristic Leaching Procedure*[1]**

This is a standard regulatory test intended to determine the potential mobility of contaminants in a liquid or solid under simulated landfill conditions. Tests are run in duplicate and analyzed for mercury content.

UC Constant pH Based Leaching

Constant pH leaching tests are a means to determine the effect pH has on the stability of a waste. The constant pH procedure was developed at the University of Cincinnati and is attached as Appendix B. Separate project specific pH leaching procedures are provided for untreated and treated surrogate to accommodate QC specific to the number of samples leached. Samples are leached in a constant pH solution that is adjusted to the desired pH end point. The constant pH leaching test will be run on the 6 pH values of 2, 4, 6, 8, 10 and 12. The pH will be maintained by automated systems for a 10 day period prior to leachate sampling. Three pH values 2, 8 and 12 experiments will be duplicated. The test shall include an experimental blank. All extracted samples are filtered and analyzed for mercury content.

[1] Federal Register-Volume 51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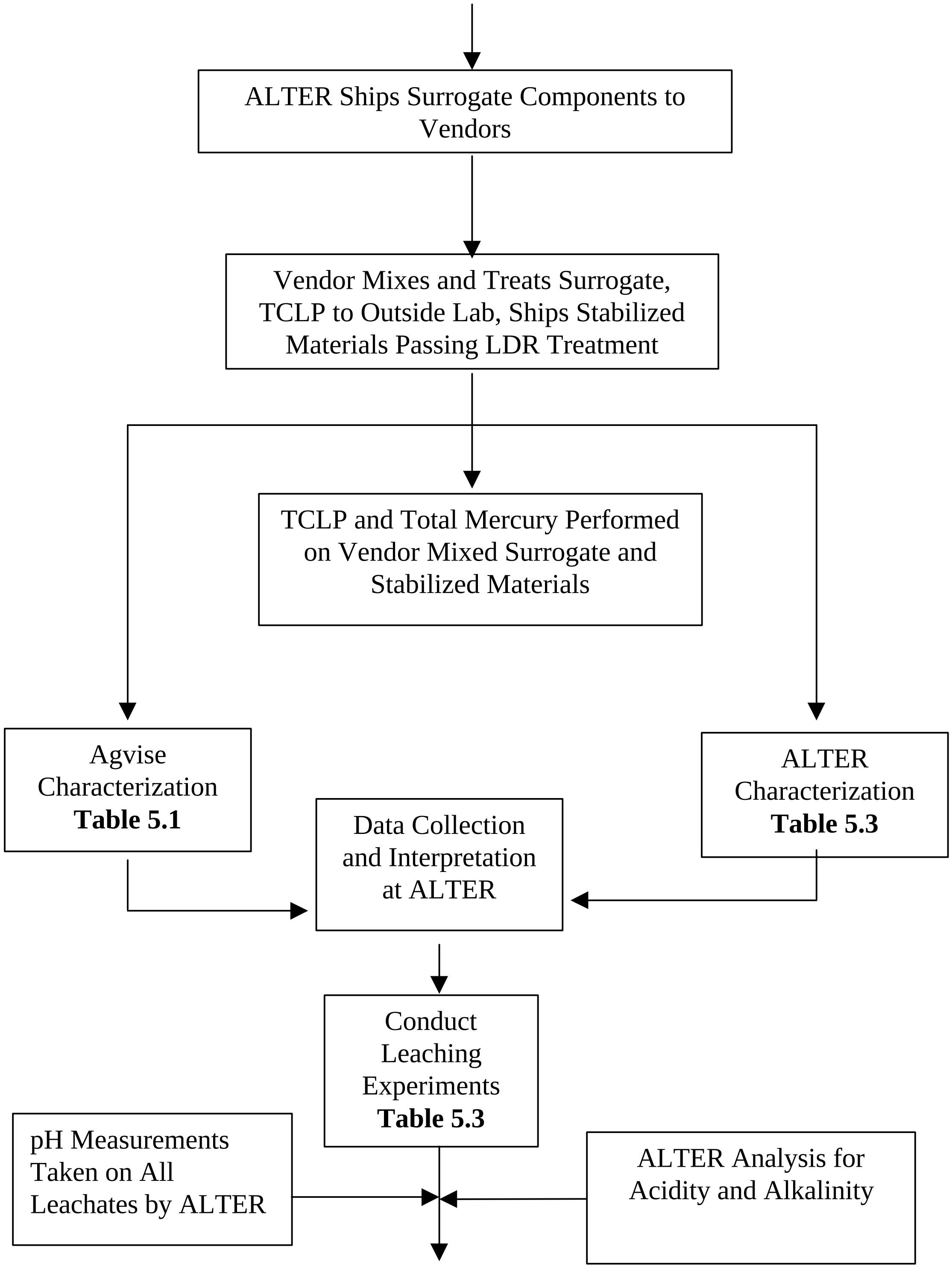
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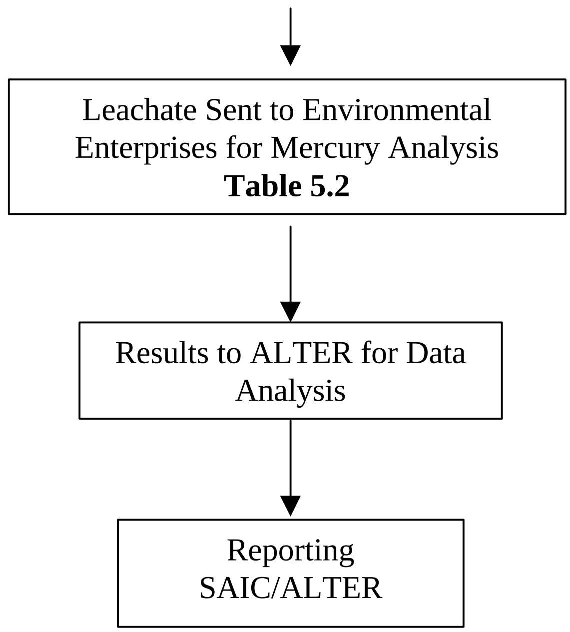


Figure 3.1 Experimental Design

4.0 Sampling Procedures

4.1 Laboratory Scale Surrogate Sludge

Preparation and sampling of the laboratory scale surrogate sludge will be performed by ALTER. The sludge will be mixed using a Hobart 5 quart mixer. The sub-samples will then be transferred to the appropriate sample containers for each test. Observations and judgements about sample homogeneity (e.g. color, texture, etc.) will be recorded in the lab notebook.

4.2 Vendor Sampling

Vendors selected by ORNL and EPA (OSW) will receive two surrogate pre-measured 100 lb. samples. Vendors will be responsible for mixing the surrogate from the components shipped by ALTER. When mixing is complete, a composite sample of approximately 1 kg will be removed from the mixed surrogate as 10 approximately 100 g random grab samples to be shipped with the treated surrogate. After treatment of the two 100 lb. surrogate batches, vendors will submit a sample of each batch to an outside lab for TCLP testing, then will return the successfully treated surrogate to ALTER for evaluation.

Each vendor will submit, for review by Mike Morris ORNL, a plan for treatment of the surrogate batches. The plan will include the following:

- Mixing method
- Sample containerization and preservation
- Process design and operating data collection.
- Total mass of treatment additives.

4.3 Sampling for Treatment Tests

All treated surrogate will be returned to ALTER for testing. The treated surrogate will be crushed if necessary to pass a 9.5 mm sieve. Crushed treated material, or material passing the 9.5 mm sieve will then be blended and sub-sampled, using a sample splitter, for each test to be performed.

4.4 Field Sample Custody

Sample custody will begin, in all cases, at the time of sample collection by placing the sample in a sealed container, or other appropriate container, in the possession of the designated laboratory or field sample custodian. A line item on the chain-of-custody record form (Appendix D) will be immediately filled out and signed by the field or laboratory sample custodian. The following information will be included when the chain-of-custody record is filled out:

Project Number	Enter the complete project number.
Project Name	Enter the project name
Samplers	Enter signature and print name of person or persons who participated in the collection of the samples listed and who should be contacted if questions arise during sample log-in. If the field sample custodian is not listed as a sampler, receipt of documentation is to be indicated.
Field Sample No.	Enter the sample numbers for each of the two 100 lb samples collected.
Date	Enter date of sample collection.
Time	Enter time of actual sample collection.
Sample Location	Enter the number of containers to be shipped for the two samples.
Remarks	Indicate special considerations for a sample (i.e., preservatives used and mass of additives).

Upon completion of all line items, or upon sample pickup, the custodian will sign, date, enter the time, and confirm completeness of all information written on the chain-of-custody record. Each individual who subsequently assumes responsibility for the sample will sign the chain-of-custody record and indicate the reason for assuming custody.

4.5 Sample Transport

Samples prepared for shipment will be packaged and labeled in compliance with current U.S. Department of Transportation (DOT) and International Air Transport Association (IATA) dangerous goods regulations. Any additional requirements stipulated by the overnight carrier will be followed.

Only a metal or plastic ice chest will be used as the outside shipping container for samples, unless otherwise specified by the shipping regulations. The outside container must be able to withstand a 4-foot drop on solid concrete in the position most likely to cause damage. Each ice chest will be lined with a 6-mil-thick plastic bag. Styrofoam or bubble wrap will be used to absorb shock. When more than one set can fit into an ice chest, each of the sets will be placed in separate plastic bags to prevent cross-contamination if breakage occurs.

After sample containers are sufficiently packaged, the 6-mil-thick plastic bag will be sealed around the samples by twisting the top and securely taping the bag closed to prevent leakage.

Chain-of-custody records and any other shipping/sample documentation accompanying the shipment will be enclosed in a waterproof plastic bag and taped to the underside of the ice chest lid.

Each ice chest prepared for shipment will be securely taped shut. This can be accomplished with reinforced or other suitable tape (i.e., strapping tape) wrapped at least twice around the ice chest near each end where the hinges are located. A label, or a business card, identifying the name and address of the responsible party will be affixed on the top of each ice chest prepared for shipment.

Sample shipping containers will be marked in accordance with DOT Regulations for Shipping Hazardous Materials (49 CFR 172) and/or IATA Dangerous Goods Regulations, 28th Edition, January 1, 1987. In addition to the complete mailing address, each ice chest must be clearly marked with “this end up” arrows on all four sides.

At the time of shipment, the sampling crew chief is to supply the following information to the ALTER Project Manager: the date on which the samples were shipped, the name of the commercial carrier, the carrier invoice number, the number of shipping containers shipped, and the expected time of arrival at the laboratory.

4.6 Laboratory Sample Custody

After the ice chests are checked for damage, the samples will be unpacked and the information on the accompanying chain-of-custody records will be examined. If the samples shipped match those described on the chain-of-custody record, the ALTER Project Manager will sign the form and assume responsibility for the samples. If problems are noted with the

sample shipment, the Project Manager will sign the form and record the problems in the "Remarks" box, and notify the ALTER QA officer.

All samples will then be logged into a sample logbook. The following information will be documented in the logbook:

- Date and time of sample receipt
- Project number
- Field sample number
- Laboratory sample number (assigned during log-in procedure)
- Sample matrix
- Sample parameters
- Storage location
- Log in person's initials

All information relevant to the samples will be secured at the end of each business day. All samples will be stored in a designated sample storage area, access to which will be limited to laboratory employees.

Samples (baseline surrogate, vendor mixed surrogate, vendor treated surrogate and leachates) will be delivered to Environmental Enterprises by the Project Manager for mercury analysis. Chain of custody records will be generated and maintained by ALTER for these samples.

5.0 Testing and Measurement Protocols

Tables 5.1 thru 5.3 list all of the methods that may be used by Agvise Laboratories, Environmental Enterprises, and the Accelerated Life Testing and Environmental Research (ALTER) Corporation in this research. Most of these are standard EPA or ASTM procedures and are referenced. Non–standard procedures are provided as appendices. Standard operating procedures for Agvise laboratories are located in Appendix E.

Samples are immediately placed in a refrigerator for storage after sampling unless a refrigerator is not required. The parameters for sample preparation and storage are listed in Table 5.4 for various matrices and analyses.

Table 5.1 Test Procedures Used by Agvise Laboratories

PROCEDURE	PRIMARY REFERENCE[1]
PHYSICAL[(2)]	
Density	NUT.02.10
Water Content	NUT.02.36
Particle size	NUT.02.32
Cation Ion Exchange Capacity	NUT.02.03
Percent Organic Matter	NUT.02.04
Cations (Magnesium, Potassium, Calcium, Sodium)	NUT.02.12

Notes:

(1) These procedures are based on Standard Methods for Soils established by the USDA and the Soil Society of America. NUT refers to Agvise's nutrient laboratory where the testing is conducted and the numerical reference refers to their standard operating procedures.

(2) A total of 250 g of raw waste is submitted for the 6 analyses. A duplicate (250g) is also submitted.

Table 5.2 Test Procedures Used By Environmental Enterprises

PROCEDURE	PRIMARY REFERENCE
Mercury (aqueous)[(1)]	SW 846 Method 7470A
Mercury (solid)[(2)]	SW 846 Method 7470A

Notes:

(1) Volume of sample available varies with test performed. Where possible, 250 ml is submitted for analysis. Test duplicates for 50% of the data points are also submitted.

(2) A total of 100 g is submitted for analysis. A duplicate is also submitted.

Table 5.3 Test Procedures Used by ALTER

PROCEDURE	PRIMARY REFERENCE	SAMPLE VOLUME/TEST
Characterization		
Leachates and Wastes		
Alkalinity	2320(1)	200g(2) / 40 ml(3)
Acidity(Variable Mass Only)	2330(1)	200g(2) / 40 ml(3)
pH (All Leachates)	4500(1)	5g(2) /Performed on gross leachate before filtration
Wastes		
Moisture Content	ASTM D 2216-80	100g(4)(5)
Particle Size	ASTM D 422-63	150g(2)
Leaching Experiments		
TCLP	Federal Register Volume 51	200g(2)
UC Constant pH Leaching	Appendix B	250g(2)

Notes:

(1) Standard Methods for the Examination of Water and Wastewater, 18th ed. 1992

(2) Minimum Dry Solids Required.

(3) Minimum Leachate Required

(4) Minimum Raw Waste Required

(5) Procedure Modified – for all wastes dry in hood at room temperature, 72°F.

Table 5.4 Sample Handling and Storage Conditions

ANALYTE	SAMPLE CONTAINER	SAMPLE CONTAINER PREPARATION	SAMPLE CONTAINER PRESERVATION	SAMPLE HOLDING TIME
Acidity	400 ml poly-ethylene beakers	One Time Use	N/A(1)	N/A(1)
Alkalinity	400 ml poly-ethylene beakers	One Time Use	N/A(1)	N/A(1)
Mercury Waste for Analysis	250 ml or larger polyethylene with screw cap	One Time Use	N/A(1)	Indefinite
Mercury Waste Stored	2-liter HDPE Jars with Teflon lids	One Time Use	None	Indefinite
Mercury Leachates	250 ml or larger polyethylene with screw cap	One Time Use	Acidify filtered aqueous samples with HNO_3 to obtain a pH <2. Keep cool (4°C)	28 days
pH	100 ml poly-ethylene with screw cap	One Time Use	N/A(1)	N/A(1)

Notes:

(1) N/A – Samples consist of leachates generated or wastes with DI water added which are measured immediately.

5.1 Calibration Procedures and Frequency

Equipment that will require periodic calibration or servicing falls into two general categories:

1. Facility support equipment
2. Laboratory testing equipment

The following paragraphs describe the types of equipment in each category and the proposed method and frequency of calibration.

Facility Support

Equipment in this category includes the Department's water deionization system, compressed air system, constant humidity moisture room (for sample storage and curing), and fume hood. All of these systems are operational and are maintained/serviced under ALTER service contracts.

Laboratory Testing Equipment Calibration

Calibration will be performed by trained personnel, or approved vendors, using the approved procedures. Identification records will be assigned and affixed to the devices and entered into supporting calibration records. The calibration frequency of each instrument will be defined within the calibration procedure. When the integrity of a product, process or sample is in question because of an out-of-calibration device, the Project Manager will be notified. Based on the evaluation performed, the extent of any non-conforming situation will be reported to the Co-PI who may specify the disposition, including re-measurement or re-test. Section 8.2 of this document discusses the corrective action scheme.

Analytical Balances

Instrument – Mettler PM 4600
Mettler B303

Calibration

The balances are calibrated daily when in use, or when moved.

Standards

Standard metric weights are used for calibration. Weights used for calibration should bracket the expected range of the sample. Calibration must be within +/- 0.01g. If variation from standard exceeds +/- 0.01 g, balance will be tagged "out of service" and will not be used. It will then be reported to Project Manager.

Cold Vapor Mercury Analysis – Environmental Enterprises, Inc.

Instrument – Varian SpectrAA20 Atomic Absorption Spectrophotometer
with VGA-76 Vapor Generation Accessory

Calibration

Prior to daily calibration and analysis, the instrument is turned on and allowed to thermally stabilize. After the lamps and optical pathway is optimized, five standards (0.5, 2, 5, 10, 40 ug/L) and a blank are analyzed in order to generate a calibration curve. The correlation coefficient ("r") is calculated and must be greater than or equal to 0.995. Immediately after calibration, the Initial Calibration Verification (ICV) secondary source check standard is analyzed. ICV acceptance criteria is +/-10% of the true value (5 ug/L). The Initial Calibration Blank (ICB) check standard is then analyzed. ICB value must be less than the reporting limit (0.5 ug/L). The Low Detection Limit (LDL) secondary source check standard is then analyzed. LDL acceptance criteria is +/-30% of the true value (0.5 ug/L). Method Blanks (MB) and Laboratory Control Samples (LCS) are then analyzed. MB value must be less than the reporting limit (0.5 ug/L). LCS acceptance criteria is +/-15% of the true value or within the suppliers certified acceptance limits for purchased soil/solid reference standards. Continuing Calibration Verification (CCV) secondary source check standards are analyzed after every 10^{th} analysis. CCV acceptance criteria is +/-20% of the true value (5 ug/L). All analytical runs must end with a CCV and CCB.

Standards

Atomic absorption standards and reference solution are ACS grade. Mercury calibration standards are purchased from Fisher Scientific. Secondary check standards are purchased from EM Science. To ensure optimum stability, each solution has a concentration of 1000 ppm. All dilutions are prepared volumetrically.

pH Meter

Instrument – Fisher Scientific Accumet pH meter 915
Fisher Scientific Accumet research AR50

Calibration

Calibration procedures for the pH meter are described in Standard Methods, 4500 –H^+ B[1]. The meter will be calibrated using a two-point calibration with certified calibration standards. Standards for calibration are pH 4 and pH 10. A pH 7 standard will be used as the check standard. The meter will be calibrated not less than twice daily, at the beginning and end of experiments, using a two point calibration protocol. Based upon comparison of pH standards with actual pH, a range of +/- 0.05 pH units is acceptable. If accuracy is not in this range, the unit will be tagged "out of service" and will not be used. It will then be reported to the Project Manger.

Standards

All calibration standards certified and are purchased from Fisher Scientific. Fresh standards are used for each calibration.

[1] Standard Methods for the Examination of Water and Wastewater, 19th ed.1995.

6.0 QA/QC Checks

The parameters routinely used to gauge data quality are precision and accuracy. Precision is defined as the reproducibility of data upon repeated analysis. Precision is monitored by comparing the results of duplicate samples. Precision objectives for all the measurements listed in Table 6.1 are presented as relative percent difference (RPD) for duplicate samples. In addition to duplicate extract and test samples, Environmental Enterprises performs a batch duplicate sample digestion and analysis at a rate of 1 for every 20 (or less) mercury samples submitted.

Accuracy is defined as the agreement of a measurement with the true value of a known traceable standard. The goal is to maintain results within the specified limits. In the study of earth or sludge materials, where numerous physical measurements are required, there are no standards of known true value against which accuracy can be estimated. Furthermore, it is clearly not feasible to “spike” a physical measurement. Therefore, accuracy for physical measurements related to percent moisture and particle size will be determined by checking the analytical balance with standard weights and bracketing the anticipated weights of the samples. Upon the development of a new method, spiked samples are analyzed and the percent recovery calculated for the analyses. This will then be an estimate of the recoveries that can be expected for the specific test system. Environmental Enterprises performs a batch spiked sample digestion and analysis at a rate of 1 for every 20 (or less) mercury samples submitted. Accuracy is further shown by the evaluation of a laboratory control sample of known value that is digested and analyzed in the same manner as the samples submitted.

This project incorporates the use of two non-standard tests for leaching of mercury-containing wastes. Procedures for these tests are provided as Appendices B & C.

Quality control with these techniques is addressed in the individual procedures. Wherever possible, reference to standards promulgated by EPA, ASTM (American Society for Testing and Materials), or COE (Corps of Engineers) will be followed. Limits of accuracy are yet to be determined and will be addressed in addenda to the Quality Assurance Project Plan as the techniques are developed.

A summary of the estimated QA objectives for precision and accuracy are presented in Table 6.1.

Table 6.1 Quality Assurance Objectives for MDL Precision and Accuracy of Chemical Analyses Performed at ALTER

Chemical / Process	Method	MDL(1)	Precision(2)	Accuracy(3)
Alkalinity	2320(4)	5 mg/l	20	75-125%
Acidity	2330(4)	5 mg/l	20	75-125%
pH	4500H^+ B (4)	--	0.02(6)	0.05(5)

Quality Assurance Objectives for MDL Precision and Accuracy of Chemical Analyses and Performed at Environmental Enterprises

Chemical / Process	Method	Reporting Limit	Precision(2)	Accuracy(3)
Mercury (aqueous)	7470A(7)	0.0005 mg/l	25	75-125%
Mercury (solids)	7470A(7)	0.05 mg/kg	25	75-125%

Notes:

(1) Method detection limit
(2) As relative percent difference (RPD) of analytical duplicates
(3) As percent recovery range
(4) Standard Methods for the Examination of Water and Wastewater, 18th ed. 1992
(5) As bias limits
(6) Expressed in pH units as limits for deviation of check standards from true value
(7) Test methods for evaluating solid waste use SW-846

6.1 Calculations of Data Quality Indicators

Precision

Precision is measured by running two or three replicate analyses. When duplicates are analyzed the precision will be expressed in terms of the Relative Percent Difference (RPD).

$$RPD = \frac{|D1 - D2|}{(D1 + D2)/2} \text{x} 100$$

where: RPD = Relative Percent Difference

D1 = Duplicate result 1

D2 = Duplicate result 2

When three samples are analyzed, precision will be reported in terms of the standard deviation and/or the coefficient of variation (relative standard deviation).

$$s = \sqrt{\frac{\sum_{i=1}^{n} \left(X_i - \overline{X}\right)^2}{(n-1)}}$$

where: s = Standard deviation

n = Number of replicates

X_1= Replicate result

$\overline{X}$ = Mean of the replicate measurements

$$CV = \frac{s_x(100)}{\overline{X}}$$

where: CV = Coefficient of variation

s = Standard deviation

$\overline{X}$ = Mean of replicate results

Accuracy

Accuracy is the defined as the degree of agreement between a measurement and an accepted reference value. For some parameters, accuracy will be gauged through analysis of reference standards. This of course depends on whether or not a reference standard exists for a given analysis. Wet chemical waste analyses have reference standards for most common parameters. Reference standards have a known true value and an acceptable range of values (usually three standard deviations established from inter-laboratory testing of the standards). When accuracy is based on reference standards, it is the accuracy objective to be within this acceptable range of values. Since analysis of reference standards estimates the accuracy of the measurement process, they may or may not truly evaluate the accuracy of the unknown sample data. When applicable, spiked samples will be analyzed to estimate unknown accuracy. In these cases, the accuracy objective is expressed in terms of maximum acceptable deviation from 100 % recovery. Percent recovery is defined as follows:

$$\%R = \frac{Sp - s}{C} \text{x}100$$

where: %R = Percent recovery

Sp = Spiked sample concentration

S = Unspiked sample concentration

C = Concentration of spike added

6.2 Internal Quality Control Checks, Performance, and System Audits

The internal quality control checks (Table 6.2) routinely implemented with analytical testing are method blanks, replicate samples, and QC standards. The following discussions describe each type of QC that is applied to the testing.

Experimental test blanks pertain only to the leaching or chemical characterization tests. These blanks are deionized water or a standard leachant, as outlined in a specific test protocol, taken through the entire equipment cleaning/sample leaching procedure or sample preparation and analysis routine. When steps in the leaching procedure call for re-use of a piece of equipment during the procedure cleaning between samples is required and blanks are collected to determine if any cross contamination has occurred. Should test blank results indicate any amount of detectable contamination, samples will be re-analyzed if possible. If this is not possible, results of the blank will be reported along with the results from the samples. Test blanks are run at a frequency of 1 for every 10 samples analyzed. If a set of tests is run on less than 10 samples, then at least 1 blank is run for each test. Each Environmental Enterprises, Inc. analytical batch consists of 1 test blank, 1 laboratory control sample and up to 20 samples. One of these samples in each batch is duplicated and spiked.

A minimum of 50% duplicate samples are run on all leaching tests. These are individual samples that are tested in parallel. The replicate analyses provide a measure of the variability (precision) of the entire testing and measurement process. Table 6.2 indicates the type and frequency of QC checks.

QC standards are samples of a known concentration which have been prepared from an independent source. This type of analysis is useful for verifying calibration of a particular system. QC Standards are analyzed on several of the chemical characterization tests. Table 6.3 indicates those tests where QC Standards are applicable and the frequency required.

Other internal quality control considerations include the following:

(1) All chemicals used in leaching procedures are reagent grade or higher purity (e.g. samples for metals analyses from leachate are acidified with re-distilled nitric acid). These chemicals are dated when received.

(2) Water used in all leaching tests is ASTM Type I or II as appropriate to the specific test.

The QA officer will participate throughout the testing and analysis cycles as was noted in Section 2. Performance and system audits will be handled by external means. ALTER will participate as required by EPA. As of now, no audits are scheduled.

Table 6.2 Quality Control Checks

QUALITY CONTROL CHECKS	FREQUENCY
Analytical Method Blanks	1 for every 10 samples(1)
Experimental Test Blanks	Leachant used in Specific Test
Calibration Standards	Daily
Analytical Duplicate	1 duplicate for every 10 samples(1)
Test Duplicate (pH Based Leaching)	Required for 50% of data points
Test Duplicate (TCLP)	Each sample duplicated
Spiked Samples	1 for every 10 samples(1)

(1) Note: If less than 10 samples are analyzed in any grouping, 1 blank, 1 duplicate, and 1 spike are required.

Table 6.3 QC Standards

TEST	STANDARD USED	FREQUENCY
Alkalinity	Na_2CO_3	1 time/test day prior to analysis
Acidity	NaOH	1 time/test day prior to analysis
pH	pH 10.0 Calibration Standard pH 7.0 Check Standard pH 4.0 Calibration Standard	Beginning and end of each operating day
Mercury	$HgNO_3$	After every 10 samples

7.0 Data Reduction, Validation and Reporting

All results will be reduced to the appropriate reporting units (designated in the Standard Procedures) by the analyst performing the test. Calculations are prepared by computer and are checked by the analyst for gross error and miscalculation. Results are averaged and the mean and the standard deviation or range are calculated. All data is reviewed by the Project Manager prior to reporting. All data points are reported along with the mean and appropriate estimations of variability. All data generated by ALTER will be retained for five years.

Raw data is collected from the instruments and entered into spreadsheets for final data calculations. The ALTER QA officer determines whether or not data have met QA objectives. Spot recalculation will be made by the QA officer to check for incorrect calculations. Approximately 10 % of the data will be checked for calculation error by the QA officer. Any data not meeting stated objectives are brought to the attention of the appropriate Project Manager. The Project Manager determines whether results are indicative of a problem or if it is simply a statistical outlier. Suspect data will be excluded from the mean and reported individually as a suspect data point. At no time will data be discarded. A data report will be reviewed by the Project Manager for overall technical review. Other validation procedures executed by the QA officer and/or Project Manager include making sure proper testing procedures are followed, adequate documentation is maintained and spot checks of calculations. The Project Manager and the QA officer review QA/QC data generated to determine whether objectives are being met and if trends in the data are indicating potential problems. If necessary, they will specify new tests based on available data - should this need be indicated from the data collected.

ALTER uses the EPA definition of Method Detection Limit (MDL) as stated in 40CFR pt136, App. B. pg.554 (7-1-91Ed): "The method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

7.1 Project Output

Environmental Enterprises will maintain all analytical data for ten years. The following QA/QC data will be provided by Environmental Enterprises Inc. as an appendix for all project analytical data:

Sample Description of ID Number	Laboratory sample ID Number
Analyses Performed	Method Reference
Analyst report	Chain of Custody
Date Prepared and Analyzed	Blank Report
Laboratory Control Sample Report	Initial Calibration Curve
Copies of Analyst Bench Sheets	Case Narrative

Monthly reports will be prepared by graduate students, reviewed by the project manager and submitted to the EPA on the 15th of every month. Distribution of the monthly report to other agencies will be at the discretion of the EPA project manager. A final report will be prepared by SAIC with input from the ALTER project manager. The final report format will be structured as follows:

1.0 Introduction

2.0 Background

Data from waste generators
Vendor process descriptions

3.0 Characterization

Data Generated by ALTER, Agvise and Environmental Enterprises as outlined in Section 3.0 of the QAPP. Characterization data will be presented in tables which will provide the parameter measured, the result and the organization responsible for the data.

4.0 Leaching

Detailed methods and results for each test will be provided as follows:

- TCLP – will be presented in a table providing mercury analysis results.
- UC Constant pH Leaching – will be presented in a table providing pH results with the corresponding mercury analysis of the leachate. The data will also be presented graphically, plotting leachate mercury concentration against pH.

5.0 Data Quality Discussion

6.0 Conclusions

- Data Interpretation
- Data based assessment of the applicability of vendor processes to treat the mercury-containing surrogate.

Modifications or deviations to standard procedures will be documented and presented in the final project report.

8.0 Assessments

8.1 Quality Assurance Reports to Management

Quality Assurance reports will be compiled by the analyst computing data, then reviewed by the Project Manager and the QA officer. Review of data quality is a continuous process. All key project personnel will meet on a weekly basis while experimental work is in progress to assure that all QA/QC practices are being followed.

Any problems and/or recommended solutions will be reported as they are encountered. It is important that all data anomalies be examined in a timely fashion in order to minimize unusable data. All QA activities will be documented in appropriate logbooks at the time of any action for later review at the routine QA meetings.

Requests for amendments of the QA Project Plan will occur only after agreement by the Project Manager and the QA officer. The Project Manager will notify EPA when a change is required and the change will be documented in writing and a copy included in the monthly report of the project. This documentation will describe the necessary changes and present the reason for the amendment request.

All principal project participants on the distribution list will receive a copy of the approved QA Project Plan. Any subsequent revisions will be distributed to these individuals as the revisions are documented. The document control format in the upper right hand corner of the page will reflect the new date and revision number.

8.2 Corrective Action Scheme

A corrective action implies the identification of a problem and subsequent elimination of the problem. Occasionally, a problem can be immediately identified by the research assistants and eliminated prior to any data collection. More often, the problem has been in existence for some time and, therefore, the need for corrective action is indicated by an out-of-control situation or unacceptable levels of completeness. In these situations, it is the responsibility of the project manager to document and oversee the corrective action process. Appropriate authorities in the problem area are contacted for assistance in the identification and elimination steps when necessary.

The corrective process is basically divided into four units:

1. Identification of the problem
2. Elimination of the problem
3. Documentation of the problem
4. Verification of the correction

In all cases, problems encountered will be dealt with immediately and eliminated as quickly as possible. No data will be generated after a problem is identified until the problem has been eliminated. If possible, suspect results generated during the existence of problem will be discarded and reanalyzed. When this is not possible or practical, suspect results will be flagged. Final disposition of such flagged, suspect results will be decided by the Project Manager in conjunction with the Co-PI or the QA officer.

Potential problems that occur and corrective action taken is outlined below:

Problem Area	Action(s)*
• Analytical Methods	
1) If the operator disagrees with any procedure or part of the analytical method	b
• Instrumental Analysis	
1) If blanks produce an erratic baseline and/or noise	b,c
2) If multiple analyses of standard(s) yield inconsistent results	b,c
3) If the calibration curve is nonlinear	b,c
4) Loss of greater than 10 % of instrument sensitivity during any given test day	b,c
5) Instruments out of calibration	a,c
• Data Review	
1) If the data is contrary to that expected	a,b
2) If the data review has not been performed within one day of analytical measurement	a,b
3) If precision and accuracy calculations are discovered to be incorrect after data has been reported	a,b

* Action Codes:

a = Notify the Project Manager; discuss with the Co-PI over that area

b = Notify the QA officer; discuss with the Co-PI

c = Adjust, repair or return the instrument to the manufacturer for repair

APPENDIX A

Acidity/Alkalinity

ALTER LABORATORY

Standard Methods for the Examination of Water and Wastewater, 1992 - 2310

ACIDITY

Acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measured value may vary significantly with the end-point pH used in the determination. Acidity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Strong mineral acids, weak acids such as carbonic and acetic, and hydrolyzing salts such as ferrous or aluminum sulfates may contribute to the measured acidity according to the method of determination.

Acids contribute to corrosiveness and influence chemical reaction rates, chemical speciation, and biological processes. The measurement also reflects a change in the quality of the source water.

1. General Discussion

a. *Principle:* Hydrogen ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard alkali. Acidity thus depends on the end-point pH or indicator used. The construction of a titration curve by recording sample pH after successive small measured additions of titrant permits identification of inflection points and buffering capacity, if any, and allows the acidity to be determined with respect to any pH of interest.

In the titration of a single acidic species, as in the standardization of reagents, the most accurate end point is obtained from the inflection point of a titration curve. The inflection point is the pH at which curvature changes from convex to concave or vice versa.

Because accurate identification of inflection points may be difficult or impossible in buffered or complex mixtures, the titration in such cases is carried to an arbitrary end-point pH based on practical considerations. For routine control titrations or rapid preliminary estimates of acidity, the color change of an indicator may be used for an end point. Samples of industrial wastes, acid mine drainage, or other solutions that contain appreciable amounts of hydrolyzable metal ions such as iron, aluminum, or manganese are treated with hydrogen peroxide to ensure oxidation of any reduced forms of polyvalent cations, and boiled to hasten hydrolysis. Acidity results may be highly variable if this procedure is not followed exactly.

b. *End points:* Ideally the end point of the acidity titration should correspond to the stoichiometric equivalence point for neutralization of acids present. The pH at the equivalence point will depend on the sample, the choice among multiple inflection points, and the intended use of the data.

Dissolved carbon dioxide (CO_2) usually is the major component of unpolluted surface waters; handle samples from such sources carefully to minimize the loss of dissolved gasses. In a sample containing only carbon dioxide-bicarbonates-carbonates, titration to pH 8.3 at 25 C corresponds to stoichiometric neutralization of carbonic acid to bicarbonate. Because the color change of phenolphthalein indicator is close to pH 8.3, this value generally is accepted as a standard end point for titration of total acidity, including CO_2 and most weak acids. Metacresol purple also has an end point at pH 8.3 and gives a sharper color change.

For more complex mixtures or buffered solutions selection of an inflection point may be subjective. Consequently, use fixed points of pH 3.7 and pH 8.3 for standard acidity determinations in waste-waters and neutral waters where the simple carbonate equilibria discussed above cannot be assumed. Bromphenol blue has a sharp color change at its end point of 3.7. The resulting titrations are identified, traditionally, as "methyl orange acidity" (pH 3.7) and "phenolphthalein" or total acidity (pH 8.3) regardless of the actual method of measurement.

c. *Interferences:* Dissolved gasses contributing to acidity or alkalinity, such as CO_2, hydrogen sulfide, or ammonia, may be lost or gained during sampling, storage, or titration. Minimize such effects by titrating to the end point promptly after opening sample container, avoiding vigorous shaking or mixing, and protecting sample form the atmosphere during titration, and letting sample become no warmer than it was at collection.

In the potentiometric titration, oily matter, suspended solids, precipitates, or other waste matter may coat the glass electrode and cause sluggish response. Difficulty from this source is likely to be revealed in an erratic titration curve. Do not remove interferences from sample because they may contribute to its acidity. Briefly pause between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

In samples containing oxidizable or hydrolyzable ions such as ferrous or ferric iron, aluminum, and manganese, the rates of these reactions may be slow enough at room temperature to cause drifting end points.

Do not use indicator titrations with colored or turbid samples that may obscure the color change at the end point. Residual free available chlorine in the sample may bleach the indicator. Eliminate this source of interference by adding 1 drop of 0.1N sodium thiosulfate ($Na_2S_2O_3$).

d. *Selection of method:* Determine sample acidity from the volume of standard alkali required to titrate a portion to a pH of 8.3 (phenolphthalein acidity) or pH 3.7 (methyl orange acidity of waste-waters and grossly polluted waters). Titrate at room temperature using a properly calibrated pH meter, electrically operated titrator, or color indicators.

Construct a titration curve for a standardization of reagents.

Use the hot peroxide procedure to pretreat samples known or suspected to contain hydrolyzable metal ions or reduced forms of polyvalent cation, such as iron pickle liquors, acid mine drainage, and other industrial wastes. Cool to room temperature before titration.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (4*b*).

e. *Sample size:* The range of acidities found in waste-waters is so large that a single sample size and normality of base used as titrant cannot be specified. Use a sufficiently large volume of titrant (20 mL or more from a 50-mL buret) to obtain relatively good volumetric precision while keeping sample volume sufficiently small to permit sharp end points. For samples having acidities less than about 1,000 mg as calcium carbonate ($CaCO_3$)/L, select a volume with less than 50 mg $CaCO_3$ equivalent acidity and titrate with 0.02N sodium hydroxide (NaOH). For acidities greater than about 1,000 mg as $CaCO_3$/L, use a portion containing acidity equivalent to less than 250 mg $CaCO_3$ and titrate with 0.1N NaOH. If necessary, make a preliminary titration to determine optimum sample size and/or normality of titrant.

f. *Sampling and storage:* Collect samples in polyethylene or borosilicate glass bottles and store at low temperature. Fill bottles completely and cap tightly. Because waste samples may be subject to microbial action and to loss or gain of carbon dioxide (CO_2) or other gasses when exposed to air, analyze samples without delay, preferably within 1 day. If biological activity is evident analyze within 6 hr. Avoid sample agitation and prolonged exposure to air.

2. Apparatus

a. *Electrometric titrator:* Use any commercial pH meter or electrometrically operated titrator that uses a glass electrode and can be read to 0.05 pH unit. Standardize and calibrate according to the manufacturer's instructions. Pay special attention to temperature compensation and electrode care. If automatic temperature compensation is not provided, titrate at 25 C, 2 C.

b. *Titration vessel:* The size and form will depend on the electrodes and the sample size. Keep the free space above the sample as small as practicable, but allow room for titrant and full immersion of the indicating portions of electrodes. For conventional-sized electrodes, use a 200-mL, tall-form Berzelius beaker without a spout. Fit beaker with a stopper having three holes, to accommodate the two electrodes and the buret. With a miniature combination glass-reference electrode use a 125-mL or 250-mL erlenmeyer flask with a two-hole stopper.

c. *Magnetic stirrer.*

d. *Pipets, volumetric.*

e. *Flasks, volumetric,* 1,000-, 200-, 100-mL.

f. *Burets, borosilicate glass,* 50-, 25-, 10-mL.

g. *Polyolefin bottle.*

3. Reagents

a. *Carbon dioxide-free water:* Prepare all stock and standard solutions and dilution water for the standardization procedure with distilled or deionized water that has been freshly boiled for 15 min and cooled to room temperature. The final pH of the water should be 6.0 and its conductivity should be <2 *m*mhos/cm.

b. *Potassium hydrogen phthalate solution,* approximately 0.05N: Crush 15 to 20 g primary standard $KHC_8H_4O_4$ to about 100 mesh and dry at 120 C for 2 hrs. Cools in a desiccator. Weigh 10.0 0.5 g (to the nearest mg), transfer to a 1-L volumetric flask, and dilute to 1,000 mL.

c. *Standard sodium hydroxide titrant,* 0.1N: Prepare solution approximately 0.1N as indicated under Preparation of Desk Reagents as indicated in Table B.

TABLE B: PREPARATION OF UNIFORM SODIUM HYDROXIDE SOLUTIONS

Normality of NaOH Solution	Required Weight of NaOH to Prepare 1,000 mL of Solution g	Required Volume of 15N NaOH to Prepare 1,000 mL of Solution mL
6	240	400
1	40	67
0.1	4	6.7

Standardize by titrating 40.00 mL $KHC_8H_4O_4$ solution (3*b*), using a 25-mL buret. Titrate to the inflection point (1a), which should be close to pH 8.7. Calculate normality of NaOH:

$$Normality = \frac{A \times B}{204.2 \times C}$$

where:
A = g $KHC_8H_4O_4$ weighed into 1-L flask,
B = mL $KHC_8H_4O_4$ solution taken for titration, and
C = mL NaOH solution used.

Use the measured normality in further calculations or adjust to 0.1000*N*; 1 mL = 5.00 mg $CaCO_3$.

d. *Standard sodium hydroxide titrant, 0.02N:* Dilute 200 mL 0.1N NaOH to 1,000 mL and store in a polyolefin bottle protected from atmospheric $C)_2$ by a soda lime tube or tight cap. Standardize against $KHC_8H_4O_4$ as directed in 3*c*, using 15.00 mL $KHC_8H_4O_4$ solution and a 50-mL buret. Calculate normality as above (3c); 1 mL = 1.00 mg $CaCO_3$.

e. *Hydrogen peroxide,* H_2O_2, 30%.

f. *Bromphenol blue indicator solution,* pH 3.7 indicator: Dissolve 100mg bromphenol blue, sodium salt, in 100 mL water.

g. *Metacresol purple indicator solution,* pH 8.3 indicator: Dissolve 100 mg metacresol purple
in 100 mL water.

h. *Phenolphthalein indicator solution, alcoholic,* pH 8.3 indicator.

i. *Sodium thiosulfate,* 0.1M: Dissolve 25 g $Na_2S_2O_3$ $5H_2O$ and dilute to 1,000 mL with distilled water.

4. Procedure

If sample is free from hydrolyzable metal ions and reduced forms of polyvalent cations, proceed with analysis according to b, c, or d. If sample is known or suspected to contain such substances, pretreat according to a.

a. *Hot peroxide treatment*: Pipet a suitable sample (see 1e) into titration flasks. Measure pH. If pH is above 4.0 add 5-mL increments of 0.02N sulfuric acid (H_2SO_4)(Section 2320B.3c) to reduce pH to 4 or less. Remove electrodes. Add 5 drops 30% H_2O_2 and boil for 2 to 5 min. Cool to room temperature and titrate with standard alkali to pH 8.3 according to the procedure of 4d.

b. *Color change:* Select a sample size and normality of titrant according to criteria of 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample into an erlenmeyer flask, while keeping pipet tip near flask bottom. If free residual chlorine is present add 0.05 mL (1 drop) 0.1*N* $Na_2S_2O_3$ solution, or destroy with ultraviolet radiation. Add 0.2 mL (5 drops) indicator solution and titrate over a white surface to a persistent color change characteristic of the equivalence point. Commercial indicator solutions or solids designated for the appropriate pH range (3.7 or 8.3) may be used. Check color at end point by adding the same concentration of indicator used with sample to a buffer solution at the designated pH.

c. *Potentiometric titration curve:*

1) Rinse electrodes and titration vessel with distilled water and drain. Select sample size and normality of titrant according to the criteria of 1*e*. Adjust sample to room temperature, if necessary, and with a pipet discharge sample while keeping pipet tip near the vessel bottom.

2) Measure sample pH. Add standard alkali in increments of 0.5 mL or less, such that a change of less than 0.2 pH units occurs per increment. After each addition, mix thoroughly but gently with a magnetic stirrer. Avoid splashing. Record pH when a constant reading is obtained. Continue adding titrant and measure pH until pH 9 is reached. Construct the titration curve by plotting observed pH values versus cumulative milliliters titrant added. A smooth curve showing one or more inflections should be obtained. A ragged or erratic curve may indicate that equilibrium was not reached between successive alkali additions. Determine acidity relative to a particular pH from the curve.

d. *Potentiometric titration to pH 3.7 or 8.3:* Prepare sample and titration assembly as specified in 4*c*1. Titrate to preselected end point pH (1*d*) without recording intermediate pH values. As the end point is approached make smaller additions of alkali and be sure that pH equilibrium is reached before making the next addition.

5. Calculation

Acidity, as mg $CaCO_3$/L

$$= \frac{[(A \times B) - (C \times D)] \times 50{,}000}{mL\ sample}$$

where:
A = mL NaOH titrant used,
B = normality of NaOH,
C = mL H_2SO_4 used (4*d*), and
D = normality of H_2SO_4.

Report pH of the end point used, as follows: "The acidity to pH __ = __ mg $CaCO_3$/L." A negative value signifies alkalinity.

6. Precision

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before analysis.

Forty analysts in 17 laboratories analyzed synthetic water samples containing increments of bicarbonate equivalent to 20 mg $CaCO_3$/L. Titration according to the procedure of 4*d* gave a standard deviation of 1.8 mg $CaCO_3$/L, with negligible bias. Five laboratories analyzed two samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of s 4*b* and 4*d*. The mean acidity of one sample (to pH 3.7) was 487 mg $CaCO_3$/L, with a standard deviation of 11 mg/L. The bromphenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

ALTER LABORATORY

Standard Methods for the Examination of Water and Wastewater, 1992 - 2320

ALKALINITY

Alkalinity of a water is its quantitative capacity to react with a strong acid to a designated pH. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural and waste-waters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values may include contributions from borates, phosphates, or silicates if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and waste-water treatment process. Raw domestic waste-water has an alkalinity less than or only slightly greater than that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2,000 to 4,000 mg calcium carbonate ($CaCO_3$)/L.

1. General Discussion

a. *Principle:* Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section LPC#301.1*a*.

For samples of low alkalinity (less than 20 mg $CaCO_3$/L) use an extrapolation technic based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.

b. *End points:* When alkalinity is due entirely to hydroxide, carbonate, or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The following pH values are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams $CaCO_3$ per liter:

Table 1. End Point pH Values

End Point pH		
	Total Alkalinity	Phenolphthalein Alkalinity
Alkalinity, mg $CaC0_3$/L:		
30	4.9	8.3
150	4.6	8.3
500	4.3	8.3
Silicates, phosphates known or suspected	4.5	8.3
Routine or automated analyses	4.5	8.3
Industrial waste or complex system	4.5	8.3

c. *Interferences:* Soaps, oily matter, suspended solids, or particulates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium. Do not filter, dilute, concentrate, or alter sample.

d. *Selection of method:* Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from 1*b*. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators.

Report alkalinity less than 20 mg $CaCO_3$/L only if it has been determined by the low-alkalinity method of 4*d*.

Construct a titration curve for standardization of reagents.

Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

e. *Sample size:* See Section LPC#301.1*e* for selection of size sample to be titrated and normality of titrant, substituting 0.02*N* or 0.1*N* sulfuric (H_2SO_4) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02*N* H_2SO_4 from a 10-mL buret.

f. *Sampling and storage:* See Section LPC#301.1*f*.

2. Apparatus

See Section LPC#301.2.

3. Reagents

a. *Sodium carbonate solution,* approximately 0.05*N*: Dry 3 to 5 g primary standard Na_2CO_3 at 250 C for 4 hrs and cool in a desiccator. Weigh 2.5g, 0.2 g (to the nearest mg), transfer to a 1-

L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

b. *Standard sulfuric acid or hydrochloric acid,* 0.1*N*: Dilute 3.0 mL conc H_2SO_4 or 8.3 mL conc HCl to 1 L with distilled or deionized water. Standardize against 40.00 mL 0.05*N* Na_2CO_3 solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watchglass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$Normality, N = \frac{A \times B}{53.00 \times C}$$

where:
A = g Na_2CO_3 weighed into 1 L flask,
B = mL Na_2CO_3 solution taken for titration, and
C = mL acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 mL 0.1000*N* solution = 5.00 mg $CaCO_3$.

c. *Standard sulfuric acid or hydrochloric acid,* 0.02*N*: Dilute 200.00 mL 0.1000*N* standard acid to 1,000 mL with distilled or deionized water. Standardize by potentiometric titration of 15.00 mL 0.05*N* Na_2CO_3 according to the procedure of 3*b*; 1 mL = 1.00 mg $CaCO_3$.

d. *Bromcresol green indicator solution*, pH 4.5 indicator: Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

e. *Mixed bromcresol green-methyl red indicator solution:* Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

f. *Methyl orange solution.*

g. *Phenolphthalein solution, alcoholic.*

h. *Sodium thiosulfate*, 0.1*M*: See Section LPC#301.3*i*.

4. Procedure

a. *Color change:* See Section LPC#301.4*a*. The color response of the mixed bromcresol green-methyl red indicator is approximately as follows: above pH 5.2, greenish blue; pH 5.0, light blue with lavender gray; pH 4.8, light pink-gray with bluish cast; and pH 4.6, light pink. Check color changes against reading of a pH meter under the conditions of the titration. Because colors are difficult to distinguish, the method is subject to relatively large operator error.

b. *Potentiometric titration curve:* Follow the procedure for determining acidity (LPC#301.4*b*), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

c. *Potentiometric titration to pre-selected pH:* Determine the appropriate end-point pH according to 1*b*. Prepare sample and titration assembly (LPC#301.4*b*). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

d. *Potentiometric titration of low alkalinity:* For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of 4*c* above, using a 10-mL microburet and 0.2*N* standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

5. Calculations

a. *Potentiometric titration to end-point pH:*

$$Alkalinity, mg\ CaCO_3/L = \frac{A \times N \times 50{,}000}{mL\ sample}$$

where:
A = mL standard acid used and,
N = normality of standard acid.

or

$$Alkalinity, mg\ CaCO_3/L = \frac{A \times t \times 1{,}000}{mL\ sample}$$

where:
t = titer of standard acid, mg $CaCO_3$/mL.

Report pH end point used as follows: "The alkalinity to pH ___ = ___ mg $CaCO_3$/L" and indicate clearly if this pH corresponds to an inflection point of the titration curve.

b. *Potentiometric titration of low alkalinity:* Total alkalinity, mg $CaCO_3$/L

$$= \frac{(2B - C) \times N \times 50{,}000}{mL\ sample}$$

where:
B = mL titrant to first recorded pH,
C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid.

c. *Calculation of alkalinity relationships:* The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principle forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate (HCO_3^-) ions are present if phenolphthalein alkalinity is less than half the total alkalinity. These relationships may be calculated by the following scheme, where *P* is phenolphthalein alkalinity and *T* is total alkalinity (1*b*):

Select the smaller alkalinity value of *P* or (*T-P*). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is *P*, the balance (*T-2P*) is bicarbonate. When the smaller value is (*T-P*), the balance (*2P-T*) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in the following table:

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Concentration
P = 0	0	0	T
P < T	0	2P	T - 2P
P = T	0	2P	0
P > T	2P - T	2(T - P)	0
P = T	T	0	0

Key: P - phenolphthalein alkalinity; T - total alkalinity.

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, LPC#316). Accurately measure pH, calculate OH^- concentration as milligrams $CaCO_3$ per liter, and calculate concentrations of CO_3^{2-} and HCO_3^- as mg $CaCO_3$/L from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2[OH^-]$$

$$HCO_3^- = T - 2P + [OH^-]$$

Similarly, if difficultly is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = 1/2[CO_3^{2-}] + [OH^-]$$

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg $CaCO_3$/L can be achieved. Forty analysts in 17 laboratories analyzed samples containing increments of bicarbonate equivalent to 120 mg $CaCO_3$/L. The titration procedure of 4*b* was used, with an end point pH of 4.5 The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.

Sodium carbonate solutions equivalent to 80 and 65 mg $CaCO_3$/L were analyzed by 12 laboratories according to the procedure of 4*c*. The standard deviations were 8 and 5 mg/L, respectively, with negligible bias. Four laboratories analyzed six samples having total alkalinities of about 1000 mg $CaCO_3$/L and containing various ratios of carbonate/bicarbonate by the procedures of both 4*a* and 4*c*. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

APPENDIX B

University of Cincinnati's Constant pH Leaching Procedure

Project Specific – Untreated Surrogate

University of Cincinnati

ALTER Facility

Constant pH Leaching Procedure

Project Specific – Untreated Surrogate

Summary

The constant pH test is a static leach test that is conducted to assess the chemical integrity of a waste form at the pH, temperature, and pressure of interest. A series of tests is commonly run to provide data on contaminant concentration as a function of pH (e.g., six tests at pH values of 2, 4, 6, 8, 10, and 12). This information is used to determine the optimum pH condition for immobilizing the contaminant.

For the mercury LDR project, two sets of pH profiles (pH 2, 4, 6, 8, 10, and 12) will be performed on untreated surrogate made at ALTER. The tests will be conducted using automated pH controllers. The specified pH will be held constant for ten days ± one hour. The leachant will be continuously stirred during the contact period with the waste form. Automated adjustments will be made with 0.1N nitric acid or 0.1N sodium hydroxide to maintain the specified pH. Prior to collection of the analytical sample at ten days, the leachate will be filtered.

Materials

Waste form
Beakers for leach tests (teflon, HDPE, or glass; 800 mL)
Magnetic stir bars
Stir plates
Constant pH controllers
Parafilm
Reagent grade nitric acid (ACS or equivalent)
Reagent grade sodium hydroxide (ACS or equivalent)
Deionized water (ASTM Type 2)
3-liter vessels for preparing leachant (HDPE or glass)
pH meter (accurate to within ±0.1 pH units)
Filters (borosilicate glass fiber; pore size of 0.7 μm)
Filter holders (teflon, HDPE, or glass; Nuclepore Corp. 425910 or 410400, or equivalent)
Polyethylene sample bottles
Laboratory balance (accurate to within ±0.01 g)
Laboratory hood or oven
Sieves (if needed)

Procedure

Prepare the waste sample: If needed, reduce the particle size of the waste sample to less than 9.5 mm in diameter. Determine the moisture content of the sample using modified ASTM D 2216

(Drying temperature is modified to 60 °C). The moisture content will be used to calculate the weight of waste sample for each pH test. 25 g of waste sample on dry basis is needed for each data point.

Prepare the leachant: Using reagent grade nitric acid and sodium hydroxide, prepare stock solutions of 0.1 N nitric acid and 0.1 N sodium hydroxide. Prepare 2 liters of leachant for each pH test by adjusting the pH of deionized water using the 0.1 N nitric acid or 0.1 N sodium hydroxide. Leachant pH values are 2, 4, 6, 8, 10, and 12.

Prepare the leach-test beakers, filter holders, and filters: Prepare a stock solution of 1.0 N nitric acid. Place the test beakers and filter holders in a bath of 1.0 N nitric acid for one hour. Remove each beaker and filter holder and rinse with 1.0 N nitric acid followed by three consecutive rinses with deionized water (minimum of 500 mL per rinse). Place the beakers and filter holders upside down on a clean, absorbent material (e.g., kimwipes) until needed. Rinse the borosilicate glass fibers with 1.0 N nitric acid followed by three consecutive rinses with deionized water (minimum of 500 mL per rinse). Assemble the filter apparatus using the filter holders and glass filters.

Prepare leach tests: Set up 11 acid washed 800 ml beakers under a hood and label them as follows:

pH-2-1 – pH 2 sample 1
pH-4-1 – pH 4 sample 1
pH-6-1 – pH 6 sample 1
pH-8-1 – pH 8 sample 1
pH-10-1 – pH 10 sample 1
pH-12-1 – pH 12 sample 1

Duplicates:
pH-2-D – pH 2 sample 2
pH-8-D – pH 8 sample 2
pH-12-D – pH 12 sample 2

Blanks:
pH-2-B – pH 2 method blank
pH-12-B – pH 12 method blank

Record the information in the log book.

Weigh out 25 ± 0.01g of dry waste sample (as calculated using the waste moisture content) for each of the 3 test beakers for each pH. Add 500mL of the appropriate pH leachant to each of the 3 test beakers for each pH and the blank beaker. Measure the leachant pH in each beaker to the nearest 0.1 pH unit and record the initial value in the log book. Place a stir bar in each beaker, cover each with parafilm and place the beakers on a stir plate. Connect constant pH controllers to each beaker and adjust for hourly pH correction. Begin stirring all beakers simultaneously, and maintain rapid stirring throughout the experiment.

Monitor and maintain pH value: The pH shall be checked manually using a pH meter on days 1, 2, 7 and 10. Record this information in the log book.

Filtration: At the conclusion of each test, the sample will be filtered prior to placing the leachate in the sample container. The leachate from each 500 mL test will be filtered through a separate 0.7 μm glass filter and collected in a polyethylene bottle. A minimum of 200 mL of filtrate must be collected for each sample. The filtrate will be acidified with nitric acid to a pH of less than 2 and stored at 4^{o} C until analyzed.

Analysis: The leachate will be analyzed for mercury content using the cold vapor atomic absorption method (SW-846 Method 7470 or Standard Method 3112B). The maximum allowable detection limit is 0.001 mg/L.

Quality Assurance Requirements: All data, including log books and analytical results, should be maintained and available for reference and inspection. Duplicates and blank sample will be analyzed for each pH value tested. Analytical work will follow all quality control measures listed in the method ant the QAPP.

APPENDIX C

University of Cincinnati's Constant pH Leaching Procedure

Project Specific – Treated Surrogate

University of Cincinnati

ALTER Facility

Constant pH Leaching Procedure

Project Specific – Treated Surrogate

Summary

The constant pH test is a static leach test that is conducted to assess the chemical integrity of a waste form at the pH, temperature, and pressure of interest. A series of tests is commonly run to provide data on contaminant concentration as a function of pH (e.g., six tests at pH values of 2, 4, 6, 8, 10, and 12). This information is used to determine the optimum pH condition for immobilizing the contaminant.

For the mercury LDR project, two sets of pH profiles will be performed on the two 100 lb samples of treated surrogate returned to ALTER from the vendors. Two pH profiles (pH 2, 4, 6, 8, 10, and 12) will be generated from batch 1 and one pH profile will be generated from batch 2. The tests will be conducted using automated pH controllers. The specified pH will be held constant for ten days ± one hour. The leachant will be continuously stirred during the contact period with the waste form. Automated adjustments will be made with 0.1N nitric acid or 0.1N sodium hydroxide to maintain the specified pH. Prior to collection of the analytical sample at ten days, the leachate will be filtered.

Materials

Waste form
Beakers for leach tests (teflon, HDPE, or glass; 800 mL)
Magnetic stir bars
Stir plates
Constant pH controllers
Parafilm
Reagent grade nitric acid (ACS or equivalent)
Reagent grade sodium hydroxide (ACS or equivalent)
Deionized water (ASTM Type 2)
3-liter vessels for preparing leachant (HDPE or glass)
pH meter (accurate to within ±0.1 pH units)
Filters (borosilicate glass fiber; pore size of 0.7 µm)
Filter holders (teflon, HDPE, or glass; Nuclepore Corp. 425910 or 410400, or equivalent)
Polyethylene sample bottles
Laboratory balance (accurate to within ±0.01 g)
Laboratory hood or oven
Sieves (if needed)

Procedure

Prepare the waste sample: If needed, reduce the particle size of the waste sample to less than 9.5 mm in diameter. Determine the moisture content of the sample using modified ASTM D 2216 (Drying temperature is modified to 60 °C). The moisture content will be used to calculate the weight of waste sample for each pH test. 25 g of waste sample on dry basis is needed for each data point.

Prepare the leachant: Using reagent grade nitric acid and sodium hydroxide, prepare stock solutions of 0.1 N nitric acid and 0.1 N sodium hydroxide. Prepare 2 liters of leachant for each pH test by adjusting the pH of deionized water using the 0.1 N nitric acid or 0.1 N sodium hydroxide. Leachant pH values are 2, 4, 6, 8 10, and 12.

Prepare the leach-test beakers, filter holders, and filters: Prepare a stock solution of 1.0 N nitric acid. Place the test beakers and filter holders in a bath of 1.0 N nitric acid for one hour. Remove each beaker and filter holder and rinse with 1.0 N nitric acid followed by three consecutive rinses with deionized water (minimum of 500 mL per rinse). Place the beakers and filter holders upside down on a clean, absorbent material (e.g., kimwipes) until needed. Rinse the borosilicate glass fibers with 1.0 N nitric acid followed by three consecutive rinses with deionized water (minimum of 500 mL per rinse). Assemble the filter apparatus using the filter holders and glass filters.

Prepare leach tests: Set up 20 acid washed 800 ml beakers under a hood and label them as follows:

pH-2-1 – pH 2 sample 1 Batch 1	pH-2-2 – pH 2 sample 1 Batch 2
pH-4-1 – pH 4 sample 1 Batch 1	pH-4-2 – pH 4 sample 1 Batch 2
pH-6-1 – pH 6 sample 1 Batch 1	pH-6-2 – pH 6 sample 1 Batch 2
pH-8-1 – pH 8 sample 1 Batch 1	pH-8-2 – pH 8 sample 1 Batch 2
pH-10-1 – pH 10 sample 1 Batch 1	pH-10-2 – pH 10 sample 1 Batch 2
pH-12-1 – pH 12 sample 1 Batch 1	pH-12-2 – pH 12 sample 1 Batch 2

Duplicates:

pH-2-D1 – pH 2 sample 2 Batch 1	pH-2-D2 – pH 2 sample 2 Batch 2
pH-8-D1 – pH 8 sample 2 Batch 1	pH-8-D2 – pH 8 sample 2 Batch 2
pH-12-D1 – pH 12 sample 2 Batch 1	pH-12-D2 – pH 12 sample 2 Batch 2

Blanks:

pH-2-B – pH 2 method blank
pH-12-B – pH 12 method blank

Record the information in the log book.

Weigh out 25 ± 0.01g of dry waste sample (as calculated using the waste moisture content) for each of the 3 test beakers for each pH. Add 500mL of the appropriate pH leachant to each of the 3 test beakers for each pH and the blank beaker. Measure the leachant pH in each beaker to the nearest 0.1 pH unit and record the initial value in the log book. Place a stir bar in each beaker, cover each with parafilm and place the beakers on a stir plate. Connect constant pH controllers to each beaker and adjust for hourly pH correction. Begin stirring all beakers simultaneously, and maintain rapid stirring throughout the experiment.

Monitor and maintain pH value: The pH shall be checked manually using a pH meter on days 1, 2, 7 and 10. Record this information in the log book.

Filtration: At the conclusion of each test, the sample will be filtered prior to placing the leachate in the sample container. The leachate from each 500 mL test will be filtered through a separate 0.7 μm glass filter and collected in a polyethylene bottle. A minimum of 200 mL of filtrate must be collected for each sample. The filtrate will be acidified with nitric acid to a pH of less than 2 and stored at 4^{o} C until analyzed.

Analysis: The leachate will be analyzed for mercury content using the cold vapor atomic absorption method (SW-846 Method 7470 or Standard Method 3112B). The maximum allowable detection limit is 0.001 mg/L.

Quality Assurance Requirements: All data, including log books and analytical results, should be maintained and available for reference and inspection. Duplicates and blank sample will be analyzed for each pH value tested. Analytical work will follow all quality control measures listed in the method and the QAPP.

APPENDIX D

Chain of Custody

ALTER Corporation

CHAIN OF CUSTODY RECORD

Page ______ of ______

PROJECT NAME PROJECT NO.

COMPANY

ADDRESS (NUMBER) (STREET) (CITY) (STATE) (ZIP CODE)

PHONE ( ) COMPANY CONTACT

SAMPLE NO.	DATE	TIME	COMPOSITE	GRAB	SAMPLE LOCATION	NO. OF CONTAINERS									REMARKS

RELINQUISHED BY:	DATE/TIME:	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME:	REMARKS:
RELINQUISHED BY:	DATE/TIME:	RECEIVED BY:	RECEIVED FOR LABORATORY BY:		

APPENDIX E

Standard Operating Procedures for Agvise Laboratories

METHOD SUMMARY FOR SOIL ANALYSIS

TESTING LABORATORY: **AGVISE LABORATORIES, INC.**
P.O. BOX 510; Highway 15
Northwood, ND 58267
(701)-587-6010

The following is a summary of analytical methods used by AGVISE Laboratories in the determination of soil characteristics and nutrient content. Analytical data of some or all of these analytical methods are presented based upon the testing requested by the firm submitting the soil specimens.

Chemical Properties

Carbonates - Determined by gravimetric loss of carbon dioxide (NUT.02.14).

Cation Exchange Capacity – Determined by summing the cations with hydrogen (NUT.02.03). The cations of Magnesium, Potassium, Calcium, and Sodium are determined by extraction with 1.0 N ammonium acetate (NUT.02.12). Hydrogen is determined by measuring the pH of the soil in Adams-Evans Buffer Solution (NUT.02.11).

Nitrogen, %Total – Determined by the Kjeldahl method (NUT.02.15).

Organic Carbon % - Determined by the Walkley-Black Procedure (NUT.02.20).

Organic Matter % - Determined by the Walkley-Black Procedure (NUT.02.09) in soils with less than 10% organic matter. Determined by the loss of weight on ignition procedure (NUT.02.04) in soils with a 10% or more organic matter.

pH – Determined with a pH electrode in a 1:1 soil:water suspension (NUT.02.05) except when specified by state regulations to use a saturated paste (NUT.02.39).

Phosphorus – Determined by the Olsen method (NUT.02.07).

Soluble Salts – Determined using a conductivity meter in a 1:1 soil:water suspension (NUT.02.19).

Physical Properties

% Gravel – Determined by dry sieving and weighing the fraction over 2 mm (NUT.02.16).

% Sand, Silt, and Clay – Determined by hydrometer method (NUT.02.06) or by pipette method (NUT.02.56).

Sand Particle Size – Determined by weighing fractions obtained by wet sieving (NUT.02.32).
Bulk Density – Disturbed bulk density is determined by weighing a known volume of dried and ground soil (NUT.02.10). Core or non-disturbed bulk density is determined by weighing a known volume of an intact, dried soil core (NUT.02.02).

Water Holding Capacity and Water Relations

Moisture % - Determined by gravimetric loss upon drying (NUT.02.36).

Saturated Hydraulic Conductivity – Determined by using the constant head method and measuring the rate of flow of water through a saturated soil column (NUT.02.34).

Water Infiltration Rate – Determined by using the constant head method and measuring the length of time from water application to production of a leachate from a soil column (NUT.02.35).

Water Holding Capacity – Determined by measuring the moisture remaining when saturated soil is placed under 1/3 or 0.10 bar pressure (NUT.02.08).

Water Holding Capacity – Determined by measuring the moisture remaining when saturated soil is placed under 15 bar pressure (NUT.02.13).

All of the above methods are detailed in the current analytical SOPs used by AGVISE Laboratories' Characterization testing laboratory.

NUT.05.01. Long Term Storage of Soil and Water Characterization Specimens: According to this Sop, soil characterization samples will be retained by AGVISE Laboratories for at least two years before disposal and water characterization samples will be retained for a period of 60 days before disposal.

Adm.05.01. Archivist Duties and Archiving Procedures: This SOP states that copies of soil and water characterization reports, original COC's and original raw data will be archived within 60days after the signature by the analytical investigator. Hard copies generated by computer will be archived weekly, and supplemental data will be archived annually.

QAU.08.01. Quality Assurance Inspections of Facilities, Studies, and Processes for GLP Compliance: Method inspections will be performed on a regular basis at AGVISE Laboratories, Inc. For soil characterization, two methods will be inspected per month and one water characterization inspection will be conducted per month. An annual facility audit will be performed by AGVISE Laboratories, Inc. Quality Assurance Unit.

All of the above methods are detailed in the current analytical SOP's used in AGVISE Laboratories' characterization laboratory.

APPROVED BY
ANALYTICAL INVESTIGATOR: ______________________________________
Robert L. Deutsch, Soil Scientist **Date**

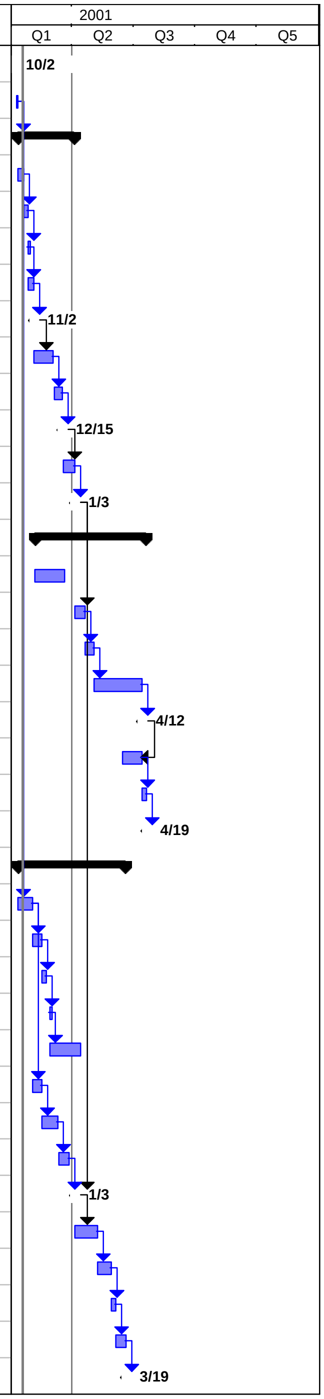
APPENDIX F

Project Schedule

Mercury >260 ppm Surrogate Sludge Testing Program Schedule

Date: 10/18/00, Revision 0, Page 1 of 2

ID	Task Name	Duration	Start	Finish	Responsible
1	**Start**	**0 days**	**Mon 10/2/00**	**Mon 10/2/00**	
2	Kick-Off Meeting	2 days	Tue 10/10/0C	Wed 10/11/00	
3	**QA Task**	**55 days**	**Thu 10/12/00**	**Wed 1/3/01**	**LR**
4	Revise Draft QA plan	5 days	Thu 10/12/0C	Wed 10/18/00	LR
5	Review Draft QA plan	5 days	Thu 10/19/0C	Wed 10/25/00	All
6	Phone Call Meeting	1 day	Thu 10/26/0C	Thu 10/26/0C	LR, Vega, MC
7	Revise Draft QA plan	5 days	Fri 10/27/00	Thu 11/2/0C	LR
8	**Submit Draft plan to EPA**	**0 days**	**Thu 11/2/00**	**Thu 11/2/00**	**LR**
9	EPA Revise & Comment plan	19 days	Fri 11/3/00	Fri 12/1/00	EPA, LR
10	Revise/Settle Comments to plan	10 days	Mon 12/4/00	Fri 12/15/00	LR
11	**Submit Plan for Final Approval to EPA**	**0 days**	**Fri 12/15/00**	**Fri 12/15/00**	**LR**
12	Plan Reviewed/Approved by EPA	10 days	Mon 12/18/00	Wed 1/3/01	EPA, LR
13	**QA Plan Approved**	**0 days**	**Wed 1/3/01**	**Wed 1/3/01**	**LR**
14	**Surrogate Testing**	**113 days**	**Mon 11/6/00**	**Thu 4/19/01**	**LR**
15	Purchase bench scale testing materials	30 days	Mon 11/6/00	Tue 12/19/0C	LR
16	Go/No-Go Surrogate test	10 days	Thu 1/4/01	Thu 1/18/01	LR
17	Reformulate surrogate (if necessary)	10 days	Fri 1/19/01	Thu 2/1/01	LR
18	Extended surrogate testing	50 days	Fri 2/2/01	Thu 4/12/01	LR
19	**Complete Extended Surrogate Testing**	**0 days**	**Thu 4/12/01**	**Thu 4/12/01**	**LR**
20	Purchase raw materials for vendor kits	20 days	Fri 3/16/01	Thu 4/12/01	LR
21	Make up vendor surrogate waste kits	5 days	Fri 4/13/01	Thu 4/19/01	LR
22	**Ship Surrogate Waste Kits to Vendors**	**0 days**	**Thu 4/19/01**	**Thu 4/19/01**	**LR**
23	**Procurement Process**	**107 days**	**Thu 10/12/00**	**Mon 3/19/01**	**MM**
24	Prepare CBD announcement	15 days	Thu 10/12/0C	Wed 11/1/00	MM
25	Review & Comment CBD announcement	10 days	Thu 11/2/0C	Wed 11/15/00	All
26	Revise CBD announcement	5 days	Thu 11/16/0C	Wed 11/22/00	MM
27	**Issue CBD Announcement**	**1 day**	**Mon 11/27/00**	**Mon 11/27/00**	**MM**
28	Vendor responses to CBD	30 days	Tue 11/28/0C	Thu 1/11/01	Vendors
29	Prepare draft SOW & RFP	10 days	Thu 11/2/0C	Wed 11/15/00	MM
30	Review & Comment SOW & RFP	15 days	Thu 11/16/0C	Fri 12/8/00	All
31	Revise SOW & RFP	10 days	Mon 12/11/00	Tue 12/26/0C	MM
32	**Issue SOW & RFP to Vendors**	**0 days**	**Wed 1/3/01**	**Wed 1/3/01**	**MM**
33	Vendor Response	22 days	Thu 1/4/01	Mon 2/5/01	Vendor
34	Review Proposals	15 days	Tue 2/6/01	Mon 2/26/01	All
35	Vendor best & final proposal	5 days	Tue 2/27/01	Mon 3/5/01	Vendor
36	Contract awards to vendors	10 days	Tue 3/6/01	Mon 3/19/01	MM
37	**Contracts Awarded to Vendors**	**0 days**	**Mon 3/19/01**	**Mon 3/19/01**	**MM**



Mercury >260 ppm Surrogate Sludge Testing Program Schedule

Date: 10/18/00, Revision 0, Page 2 of 2

ID	Task Name	Duration	Start	Finish	Responsible
38	**Vendor Testing**	**105 days**	**Tue 3/20/01**	**Fri 8/17/01**	**MM**
39	Prepare test plans	20 days	Tue 3/20/01	Mon 4/16/01	Vendor
40	Review & comment test plans	5 days	Tue 4/17/01	Tue 4/24/01	all
41	**Test Plans Approved**	**0 days**	**Tue 4/24/01**	**Tue 4/24/01**	**MM**
42	Receive surrogate waste kits	5 days	Wed 4/25/01	Tue 5/1/01	LR
43	**Begin Vendor Testing**	**0 days**	**Tue 5/1/01**	**Tue 5/1/01**	**Vendor**
44	Bench scale testing	20 days	Wed 5/2/01	Wed 5/30/01	Vendor
45	Two-100 lb batch scale testing	10 days	Thu 5/31/01	Wed 6/13/01	Vendor
46	**Complete Vendor Testing**	**0 days**	**Wed 6/13/01**	**Wed 6/13/01**	**Vendor**
47	Waste form (WF) analysis	10 days	Thu 6/14/01	Wed 6/27/01	Outside lab
48	Package & ship WF to U of C	5 days	Thu 6/28/01	Fri 7/6/01	Vendor
49	Prepare draft report	30 days	Mon 7/9/01	Fri 8/17/01	Vendor
50	**Vendor Report to DOE**	**0 days**	**Fri 8/17/01**	**Fri 8/17/01**	**Vendor**
51	**Waste Form (WF) Evaluation**	**75 days**	**Fri 7/6/01**	**Mon 10/22/01**	**LR**
52	Receive Waste Forms From Vendors	0 days	Fri 7/6/01	Fri 7/6/01	LR
53	Sample preparation	5 days	Mon 7/9/01	Fri 7/13/01	LR
54	WF TCLP testing 3 vendors	15 days	Mon 7/16/01	Fri 8/3/01	LR
55	WF pH testing for 3 vendors	70 days	Mon 7/16/01	Mon 10/22/01	LR
56	WF variable mass testing for 3 vendors	15 days	Mon 7/16/01	Fri 8/3/01	LR
57	Complete WF Testing	0 days	Mon 10/22/01	Mon 10/22/01	LR
58	**Final Report**	**40 days**	**Tue 10/23/01**	**Wed 12/19/01**	**SAIC**
59	Prepare Final Draft Report	20 days	Tue 10/23/01	Mon 11/19/01	SAIC
60	Review & Comment Draft Report	10 days	Tue 11/20/01	Wed 12/5/01	All
61	Revise & issue final report	10 days	Thu 12/6/01	Wed 12/19/01	
62	**Issue Final Report**	**0 days**	**Wed 12/19/01**	**Wed 12/19/01**